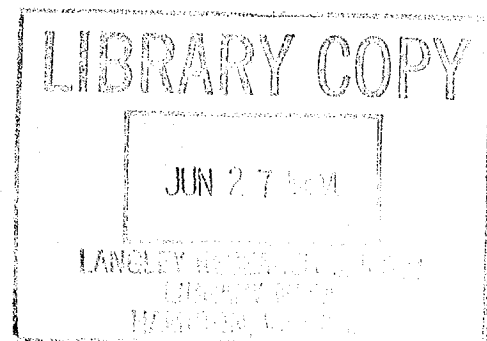NASA Technical Memorandum 106522

Frictional Behavior and Adhesion of Ag and Au Films Applied to Aluminum Oxide by Oxygen-Ion Assisted Screen Cage Ion Plating (SCIP)

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SUMMARY

A modified dc-diode ion plating system, by utilizing a metallic screen cage as a cathode, is introduced for coating nonconductors such as ceramics. Screen cage ion plating (SCIP) is used to apply Ag and Au lubricating films on aluminum oxide surfaces. This process has excellent ability to coat around corners to produce three-dimensional coverage of the substrate. A dramatic increase in adhesion is achieved when plating is performed in a reactive 50 percent O_2–50 percent Ar glow discharge compared to the adhesion when plating is performed in 100 percent Ar. The presence of oxygen ion assistance contributes to the excellent adhesion as measured in a pull-type adhesion tester. The Ag and Au film adhesion is significantly increased (>70MPa) and generally exceeds the cohesion of the substrate such that portions of the alumina are pulled out.

The deposited Ag and Au lubricating films not only reduce the coefficient of friction during sliding contact, but also reduce the surface tensile stresses that contribute to undesirable subsurface cracking and subsequently to severe wear. The strong adhesion of Ag and Au films to alumina imparted by reactive SCIP is of critical importance in achieving low and steady friction coefficients and low wear.

INTRODUCTION

Surface modifications to ceramic surfaces for tribological applications has become a subject of critical importance. Ceramic elements such as ball bearings, valve components, piston rings, and cylinder liners are increasingly being specified for engines which have to withstand severe service operating conditions such as high speeds, loads, and temperatures. It is well known, that unlubricated ceramics are unacceptable for commercial sliding and rolling applications. Therefore, lubrication is required before they become tribologically useful. One way to reduce the friction of ceramics is to coat them with soft metallic films such as Ag or Au.

The foremost requirement for the use of soft, metallic, lubricating films is strong adhesion. Since Ag and Au films do not form stable oxides, their adhesion to Al_2O_3 surfaces is poor, therefore deposition processes have to be selected which favorably affect the metal-Al_2O_3 interface. Recently, adherent Ag films have been achieved on Al_2O_3 surfaces by Ion Beam Enhanced Deposition (IBED) (refs. 1 and 2) and by sputter deposition where an interlayer of Ti or Cr is used between the ceramic and the Ag film (refs. 3 and 4). This method of Ti and Ag deposition is a two step process.

The present paper describes a relatively simple, one-step, economical process for applying adherent metal films (in this case silver or gold) onto the surfaces of nonconducting ceramics. This process is essentially an improved modification of the screen cage ion plating process (SCIP) that was described in reference 5. The modification consists of using a reactive glow discharge ion source composed of 50 percent O_2–50 percent Ar instead of pure argon as the ion source in the glow discharge plasma. The purpose of the oxygen addition is to attempt to improve adhesion of the relatively inert metals to nonconducting ceramics, while retaining the excellent "throwing power" of the SCIP method. (Throwing power is the ability to coat both line of sight and nonline of sight surfaces (three-dimensional coverage).) Most other PVD (physical vapor deposition) methods have comparatively little ability to coat nonline of sight surfaces.

The adhesion strength is measured by pull testing. Friction and wear characteristics are evaluated by scratch testing and the pin on disk friction tests are performed at 25 and 800 °C.

PRINCIPLES OF UNLUBRICATED AND LUBRICATED TRIBO-CONTACTS ON ALUMINA

According to the adhesion theory of friction (refs. 6 and 7), the frictional force, F, is proportional to the shear strength, s, and the real area of contact, A, (F = As), as shown in figure 1. For friction to be low, either A or s or both must be small. This means that the most suitable materials must have high hardness and low shear strength. However, this generally is not achievable with monolithic ceramics, where two ceramic surfaces are in contact (e.g., Al_2O_3 against Al_2O_3) as shown in figure 1(a). The frictional force is large in the absence of a low shear strength, ductile surface film. However, by using a thin layer of soft, low shear strength solid material such as Ag or Au on very smooth ceramic surfaces friction, and usually wear, can be reduced. Figure 1(b) schematically illustrates the mechanism of friction reduction with soft coatings. The aim is to confine friction losses to a thin, low shear strength film interposed between the contacting surfaces thus lowering the coefficient of friction.

Microstress distributions in static and sliding contacts of ceramics are illustrated in figures 2(a) and (b). The stresses in the static contact of a sphere against a flat are compressive within the contact circle, but are weakly tensile just outside the circle. In a sliding contact with high friction, however, high surficial tensile stresses are generated. These tensile stresses increase with load and friction coefficient and are responsible for initiating microcracks which propagate and intersect at and below the surface to produce microfractures and loose wear particles. Microfracture is a typical wear mode for unlubricated ceramics in sliding contact (ref. 8). Lowering the friction coefficient significantly increases the critical load for crack initiation and microfracture (ref. 9). One way not only to reduce friction and wear but also to increase the critical load for crack initiation and microfracture is by depositing soft adherent Ag or Au lubricating films (ref. 9). The reduction of the tensile stresses in a Ag lubricated sliding contact is qualitatively illustrated in figure 2(c). This subject is treated quantitatively in reference 9.

EXPERIMENTAL CONDITIONS

Specimens

In this investigation, optically smooth sapphire plates (0.01 μm rms) and pure alumina flats with a surface finish of 0.2 μm rms were plated with 0.3 to 0.6 μm thick Ag and Au films. Adhesion and scratch tests were performed on these specimens. Also, pure alumina (99.4 percent) disks, 6.35 cm in diameter and surface finish of 0.3 μm rms were coated with 1–4 μm thick silver and gold films using the SCIP process described below. The coated disks were tested under atmospheric conditions at 25 and 800 °C in a pin-on-disk high temperature tribotester.

Screen Cage Ion Plating (SCIP) of Ag and Au

The SCIP apparatus is shown photographically in figure 3(a) and schematically in figure 3(b). The basic system consists of a dc-diode configuration. The effectiveness of the process stems from its ability to provide high energy flux of ions and energetic neutrals which contribute to the excellent adhesion and fine, equiaxed grains of high packing density (ref. 10). In the diode ion plating process the plasma is generated by the ionizing effects of secondary electrons ejected from the cathode and the ionization of the plating species is relatively low, about 0.1 percent (ref. 11). The energetic neutrals are generated through charge transfer collisions, and they

constitute a very significant proportion of the energy carried under typical ion plating conditions. In SCIP, the ceramic specimen is suspended in a screen cage (either silver or gold) that functions as an electronic grid. The separation between the grid and the ceramic surface is critical, and generally, should be small, on the order of 6mm. If the spacing is large, a hollow cathode discharge is set up which generates excessive heating. The negative potential is applied to the screen cage. The respective metals are evaporated by resistance heating. Three different gas compositions, pure Ar, pure O_2, and a mixture of 50 percent Ar–50 percent O_2 were used. The total gas pressure for the generation of the plasma is set at a constant value of 20 mtorr. Before Ag or Au plating which is done at –4kV, 80mA and 20 mtorr, the ceramic specimens were soaked in the selected plasma at –2kV, 20mA for about two min Because of the high throwing power of ion plating, the ceramic surfaces are coated 3-dimensionally with a complete coverage. This is illustrated in figure 4 with a cross section photomicrograph of a coated alumina block. All surfaces are silver coated including the surface 180° from the silver evaporation source.

ADHESION TESTS

A commercial pull-tester (Sebastian IV) is used to obtain adhesion measurements of the Ag and Au films to the sapphire and alumina substrates. In these tests, an epoxy coated Al pin (2.7 mm in diam.) is secured with a mounting spring clip to the film and transferred to an oven for curing at 150 °C for one hr. After curing, the test pin is inserted into the instrument where the pin is pulled with an increasing force normal to the plane of the film while the load is continuously measured until failure occurs. The failure occurs either in the epoxy, at the film/ceramic interface or in the ceramic substrate. The maximum measurable strength by this test is the strength of the epoxy bond, which is about 70–75 MPa. After measuring the adhesive strength, the fractured surfaces are examined by optical microscope to determine where the rupture occurred. In this study, the adhesive strength is the load at which the pin was detached from the film or pulled out of the substrate.

SCRATCH TESTING

A commercial scratch tester (Revetest) was used to scratch the Ag coated and uncoated sapphire surfaces. The scribe was a diamond stylus with a 200 μm tip radius and a 120° cone angle. Each scratch was 10 mm long and was made at a velocity of 10mm/min The scratches were made with a constant load on the stylus. The lightest constant load was 1.6N and the loads were increased in approximately 5N increments up to 50N. The critical load, L_C, which generates cracks on uncoated and Ag coated surfaces was determined by acoustic emission and optical microscopy.

FRICTION TESTING

The Al_2O_3 disks, SCIP coated in an (Ar-O_2) glow discharge, were friction tested with bare Al_2O_3 pins which were hemispherically tipped with a 2.54 cm radius of curvature. The pin-on-disk testing was performed in a high temperature tribometer (ref. 12). The tribo-testing was done in air atmosphere under 4.9N load at 1m/sec (370 rpm) velocity for 60 min at 25 and 800 °C. After testing, the specimens were removed to measure pin and disk wear scar diameters to calculate the pin and disk wear factors.

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RESULTS AND DISCUSSION

ADHESION

The first and foremost requirement for the use of solid, lubricating films on ceramic surfaces is that the films be strongly bonded to the substrate. To assure this requirement, it is desirable to quantitatively measure the film-to-substrate bond or adhesive strength. It is very difficult to quantify such effects. In this study the pull-test technique is used strictly as a screening test to establish some quantitative measurements as guidelines. The limitations of all techniques using an epoxy bonding agent is that the maximum adhesion that can be measured must be less than the strength of the epoxy itself. The nominal strength of the epoxy is about 70 MPa.

In most of these pull tests, epoxy failure occurs or the cohesion of the substrate is exceeded, such that portions of the sapphire or alumina are pulled out, with the film still intact. The average pull test adhesive strengths for Ag and Au films plated in Ar, 50 percent Ar–50 percent O_2 and O_2 plasmas on sapphire and alumina substrates at identical plating conditions are summarized in figures 5(a) and (b). Usually, six pull tests were made on six separately plated specimens at each plating condition to determine the average adhesion strength. These results reveal that the qualitative value of film adhesion is greatly increased when the films are plated in (Ar-O_2) or O_2 glow discharge. The oxygen assisted deposition produces remarkably enhanced Ag and Au adhesion to the sapphire and alumina substrates; whereas, argon-assisted deposition results show moderate improvement for the Ag films and little or no improvement for the Au films. The results also show that the adhesive strength is the same for Ag films deposited in pure oxygen or in a mixture of 50 percent Ar–50 percent O_2. All the films deposited, except vapor deposited and Au plated in pure argon, also passed the adhesive tape pull test.

The Ag films deposited in pure oxygen plasma on sapphire are analyzed by Auger Electron Spectroscopy (AES) to determine the oxygen content. No oxygen is detected in the wall of the sputter crater produced during the film depth profile as shown in figure 6. Also, AES depth profiling traces in figure 7 verifies the absence of detectable oxygen in the film. Presently there is no experimental evidence to explain why oxygen ion bombardment promotes enhanced adhesion to the substrate.

The increased adhesion depends on the manner in which the Ag or Au "wets" or bonds to the substrate. It is surmised that the excited and ionized oxygen atoms (O_2+/O+) in the glow discharge may form metastable silver oxides on the sapphire surface which are dissolved or dissociated thus promoting an enhanced adhesion

TRIBOTESTING

A series of scratches are made on Ag coated and uncoated sapphire surfaces starting at a constant load of 1.6N and then at increased loads of approximately 5N increments. The photomicrographs in figures 8(a) and (c) from reference 9 show the onset of microfracture on uncoated and Ag coated substrates. The critical load to initiate cracks during scratch tests for uncoated sapphire is ≤5.5 N and for Ag coated sapphire, it is between 10 and 15N (ref. 9). The typical cross sectional SEM micrograph in figure 8(b) shows microstructure and grain pull-out and radial crack propagations.

For thin silver films up to about 1-μm in thickness, the results of scratch tests are in good quantitative agreement with the stress analyses presented in reference 9. These analyses predict the effect of friction on surface stresses during sliding. For thicker films of 3 to 4 μm in thickness, the critical load for crack initiation is higher than predicted. (The thicker films plastically deform during sliding, thus reducing the stress maxima).

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It has been suggested that ion bombardment during ion plating may induce compressive surface stresses and thereby improve the fracture toughness of the substrate material (ref. 13). However, the good agreement between experiment and the analyses (which does not take this possibility into account) appears to indicate that the effect of ion-induced compressive stress is not significant in this work.

The pin-on-disk friction results of oxygen assisted screen cage ion plated Ag and Au films run at atmospheric conditions under 4.9 N load at 1m/min (370 rpm) sliding velocity for 60 min at 25 and 800 °C are summarized in Table I. Unlubricated alumina disks displayed high friction coefficients of approximately 0.85 at both test temperatures. Typical friction traces obtained at 25 °C for Ag and Au plated disks are shown in figure 9. The friction coefficient is significantly reduced to about 0.32 for Ag and 0.22 for gold. This remarkable decrease by a factor of 3 to 4 over a frictional time span of 60 min further verifies the strong adherence of the coating. The pin wear factor for Ag/Al_2O_3 coated specimens is 3.06 E–07, mm^3/Nm; whereas, for Au/Al_2O_3 specimens, it is 1.37 E–09 mm^3/Nm. The preliminary results of Au coated samples displayed dramatic decrease in wear as shown by the very low pin wear factor. Additional friction tests on Au plated disks were performed in 10 min each, speed/temperature intervals (10 rpm to 370 rpm and 25 and 800 °C) as shown in Table II and plotted in figure 10. The average coefficient of friction remained at about 0.22 and the Au film displayed a high degree of frictional stability.

CONCLUSIONS

1. Screen Cage Ion Plating (SCIP) is a powerful, simple, and economic technique for plating noble metals such as Ag and Au on oxide ceramics. Strong adhesion is achieved when the plating is performed in a glow discharge that is generated in an atmosphere of 50 percent Ar–50 percent O_2 in which the ionized oxygen species are responsible for enhanced adhesion.

2. The SCIP process has superior "throwing power" compared to simple vapor deposition or sputtering processes. It is capable of coating even nonline of sight surfaces to produce "3-D" coverage of the substrate.

3. Adherent, silver lubricant coatings lower friction-induced surface tensile stresses during sliding, thereby increasing the critical load for crack initiation in brittle alumina.

4. The coating process developed in this program produces Ag and Au lubricant coatings that give low steady state friction coefficients and low wear.

ACKNOWLEDGMENT

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TABLE I.—FRICTION AND WEAR RESULTS

Test Conditions: 4.9N load, 1 m/s (370 rpm) sliding velocity, air, 60 min tests, 2.54 cm diam Al_2O_3 pin.

Disk specimen	Average friction coefficient	Pin wear factor, mm^3/N-m	Disk wear factor, mm^3/N-m
Unlubricated Al_2O_3	0.85	$1.5 \pm 0.3 \times 10^{-4}$	$4.4 \pm 0.4 \times 10^{-5}$
Ag/Al_2O_3 (25 °C)	0.32±0.03	3.06×10^{-7}	6.07×10^{-6}
Au/Al_2O_3 (25 °C)	0.22±0.03	1.37×10^{-9}	2.31×10^{-6}
Au/Al_2O_3 (800 °C)	0.28±0.03	2.7×10^{-9}	2.0×10^{-6}

TABLE II. FRICTION OF SCIP'd
Au/Al_2O_3 DISK VERSUS Al_2O_3 Pin

Test Conditions: 4.9 N load, 10 min each speed/temperature interval, in air.

rpm	25 °C	800 °C
10	0.11±0.01	0.32±0.03
50	0.15±0.02	0.30±0.02
100	0.21±0.01	0.26±0.08
175	0.21±0.02	0.23±0.02
250	0.30±0.05	0.23±0.02
370	0.32±0.05	0.23±0.01

A = Contact area
s = Shear strength
F = Frictional force
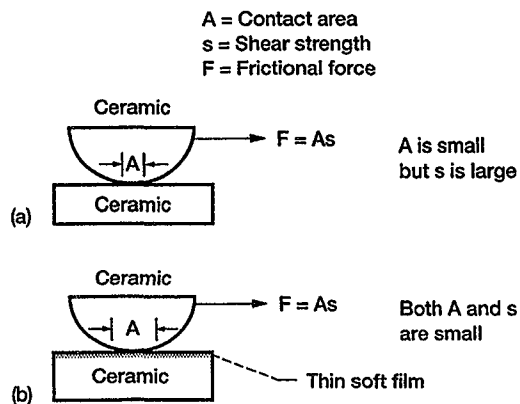
Figure 1.—Principles of ceramics in tribocontact.
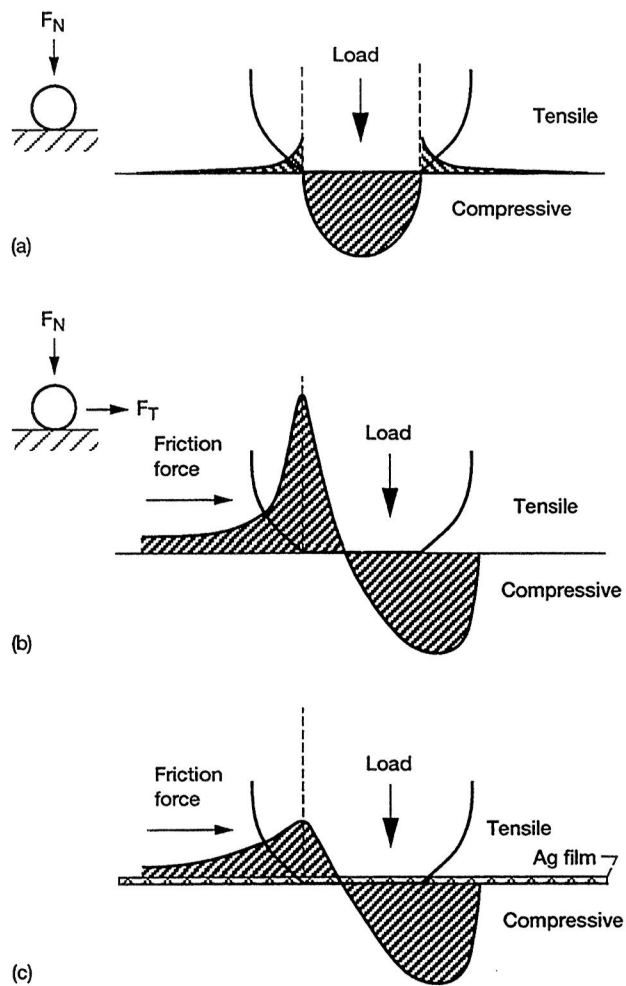
Figure 2.—Contact stress distribution during sliding on unlubricated and Ag lubricated alumina. (a) Stationary contact. (b) Sliding contact. (c) Ag lubricated sliding contact.
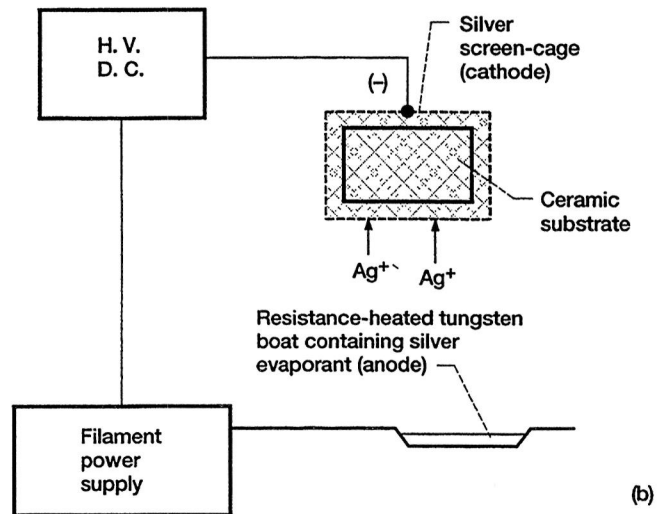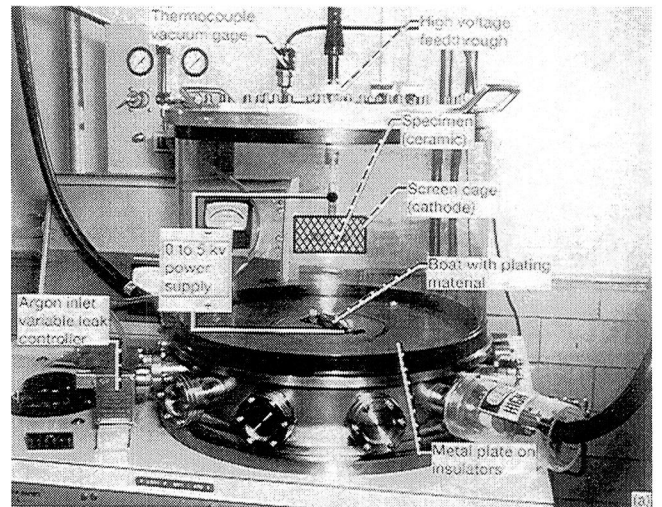
Figure 3.—(a) Screen cage ion plating chamber (SCIP). (b) Schematic for screen-cage ion plating of ceramics.
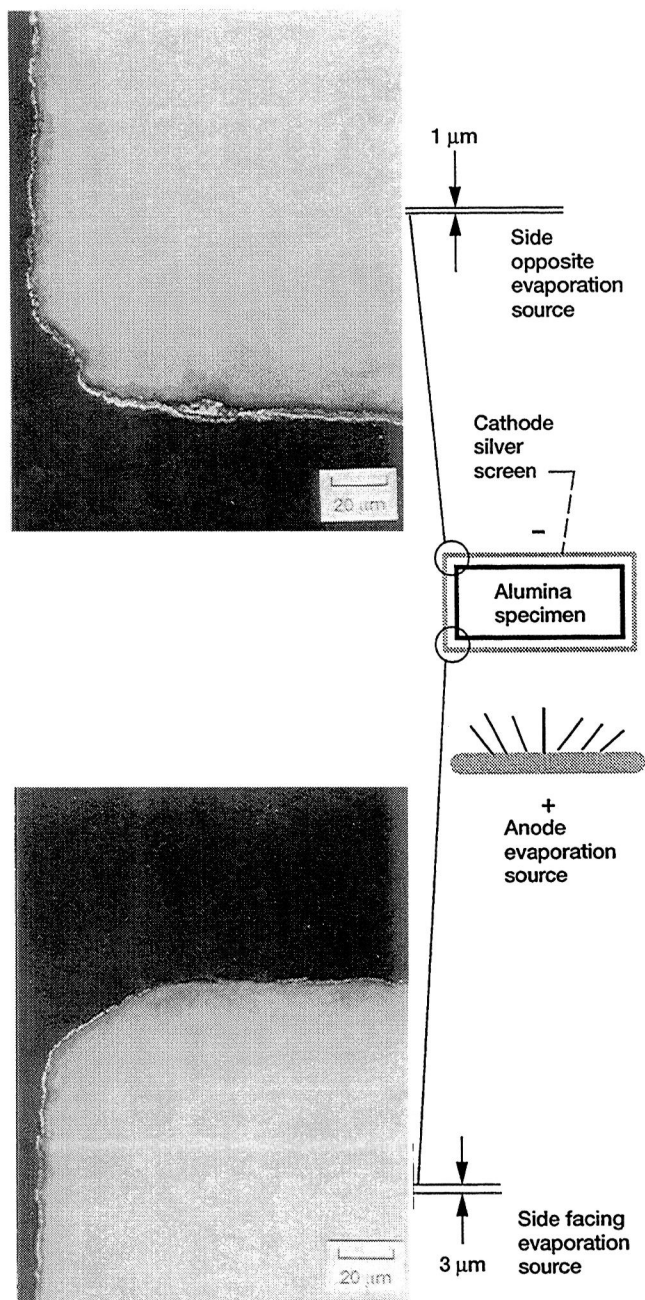
Figure 4.—Cross-section of silver-coated alumina specimen illustrating the excellent "throwing power" (complete substrate coverage) of the "SCIP" process.
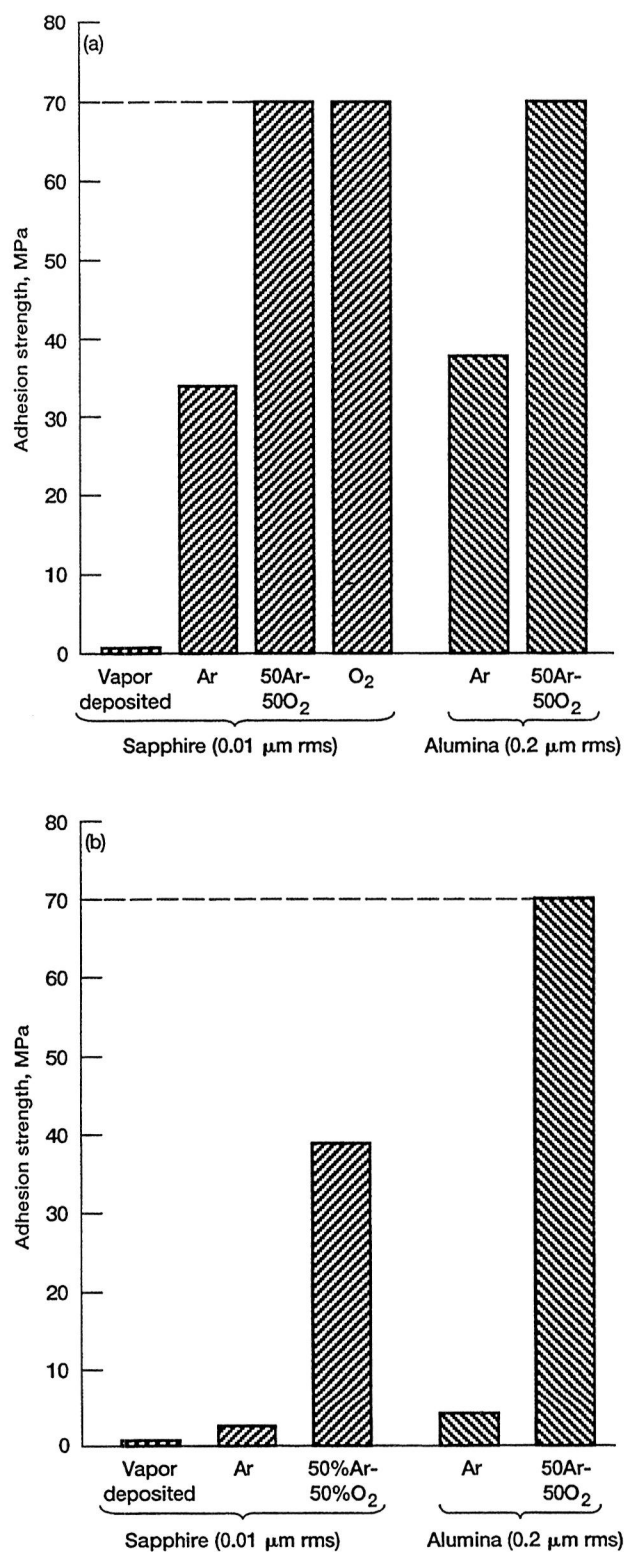

Figure 5.—Adhesion strengths of SCIP. (a) Ag films at different plasma compositions. (b) Au films at different plasma compositions. (Maximum strength of bonding agent ~70).
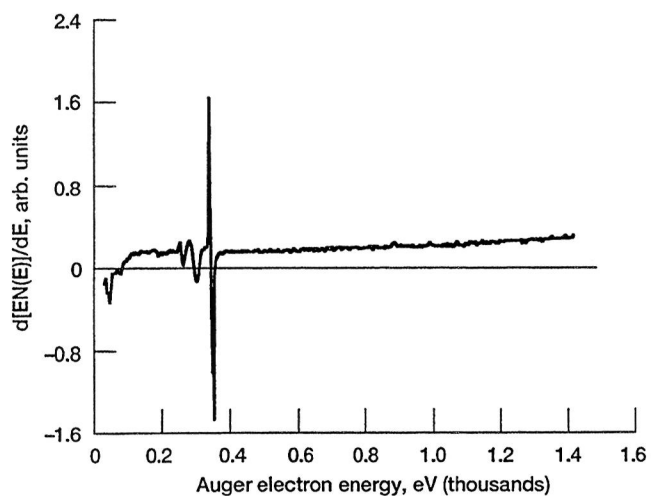
Figure 6.—Auger spectrum of sputter crater wall in Ag film SCIP'd in oxgen plasma on sapphire.
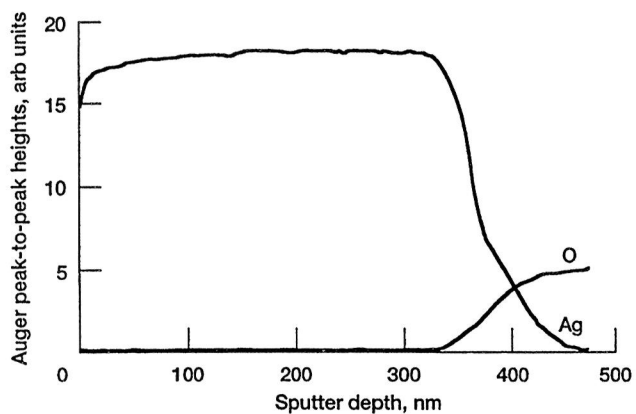
Figure 7.—Auger depth profile of Ag film on sapphire SCIP'd in oxygen plasma.

No damage

1.6 N

50 μm

Early microstructure damage

5.5 N

(a)

(b)

No damage

10.7 N

50 μm

Early microstructure damage

14.7 N

(c)
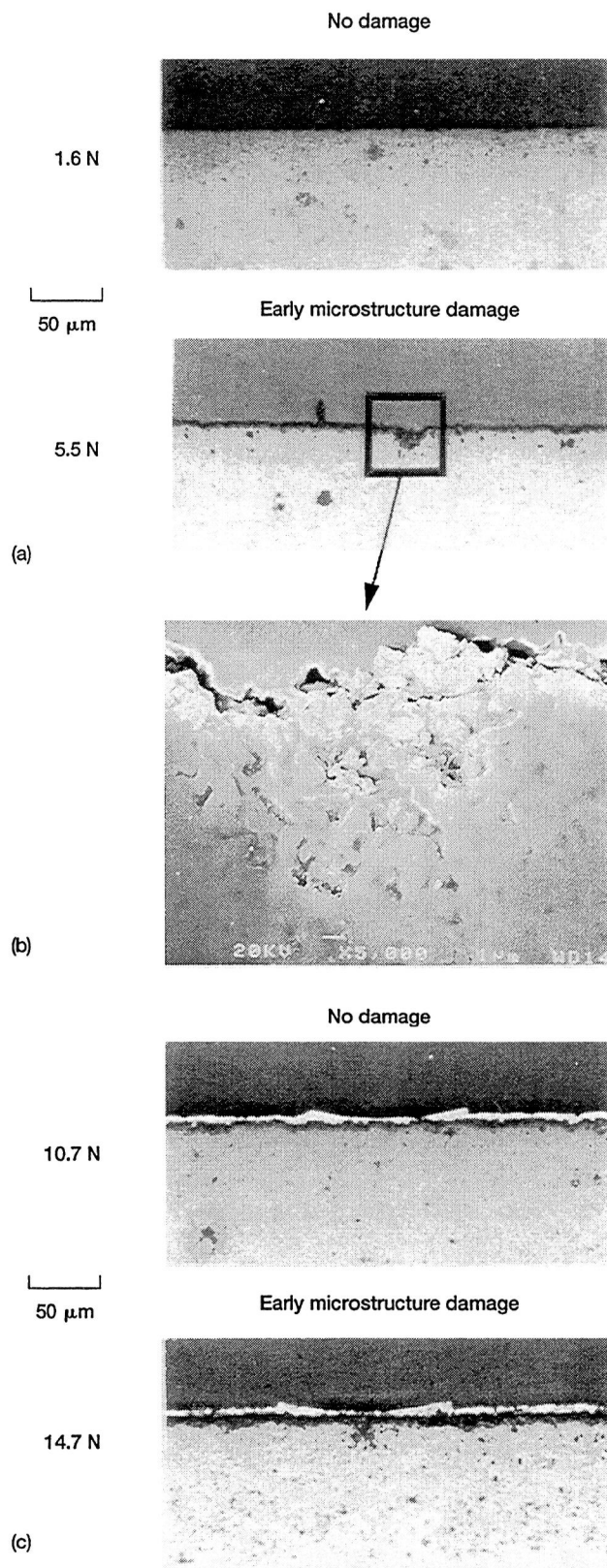
Figure 8.—Onset of microfracture and surfical damage on alumina after scratch testing. (a) Uncoated Al_2O_3. (b) Enlarged view of boxed section in part (a). (c) Ag coated.
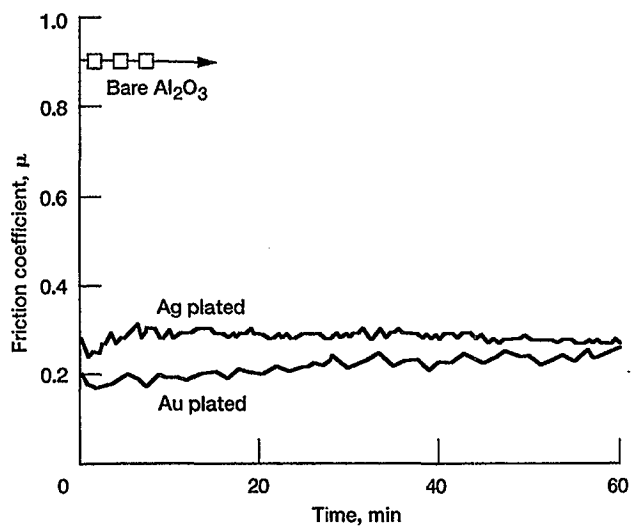
Figure 9.—Friction coefficient vs. sliding time for unlubricated and Ag and Au coated Al_2O_3. Test velocity 1m/s, load 4.9 N, atmosphere ambient at 25 °C.
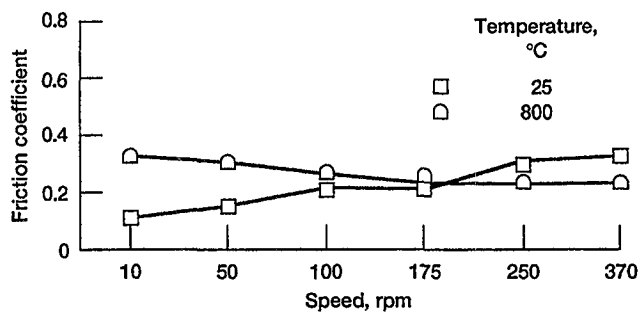
Figure 10.—Friction coefficient vs. sliding speed for SCIP'd Au on Al_2O_3.

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